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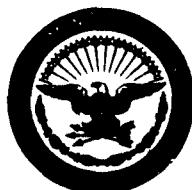
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TITLE: ION EXCHANGE MEMBRANE ELECTROLYTES

Report No. 4

Contract No. DA-36-039-SC 89197

Order No. 1074-PM-62-93-93

Task No. 3A99-09-001-02

Fourth Quarterly Progress Report, 1 Dec. 1962 to 28 Feb. 1963

U. S. Army Electronics Research and Development
Laboratory

Fort Monmouth, New Jersey

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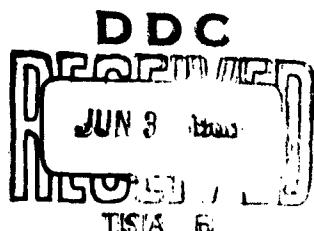
Object: To develop membrane electrolytes which permit higher power per unit of weight and volume, as well as long operational life in fuel cells.

Report prepared by H. P. Gregor, Project Supervisor

R. M. Danziger, Research Fellow

R. A. Cooper, Research Fellow

G. Brandrup, Research Assistant



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2. Purpose

The general objective of this investigation is the development of membrane electrolytes which permit higher power per unit of weight and volume, as well as long operational life in fuel cells. More specifically, this investigation resolves itself into the following specific aims:

- a. Preparation of membranes with catalysts attached to their surfaces, with ohmic resistances below 3 ohm-cm².
- b. A minimization of electroosmotic water transport, to prevent dehydration of one side.
- c. Cation and anion-exchange membranes, comprised of organic and inorganic materials for use in acid and alkaline solutions will be investigated.
- d. The materials investigated shall be characterized, where called for, by the following chemical and physical properties: specific conductivity in leached and nonleached state treated with various equilibrating solutions; capacity; moisture content; shrinkage on drying; gas permeability; temperature stability; stability in acid and alkaline solutions; stability in certain organic solvents; electroosmotic water transport. For each characterization procedure, a set of requirements has been established.
- e. The electrochemical evaluation of the membranes so prepared shall be made, using recent electrochemical techniques. This shall include: measurement of current-voltage curves of hydrogen and oxygen electrodes and their analysis with respect to activation, concentration and ohmic polarization; correlation of the extent of polarization with the physical-chemical properties

(of the membranes; study of the Tafel region and a determination of the exchange current density and the limiting current density for both anode and cathode.

3. Abstract

Additional progress has been made in the preparation of low resistance homogeneous membranes, using polystyrenesulfonic acid as the polyelectrolyte, through the use of phenolic and epoxide cross-linking agents. Several mosaic membranes have been prepared and are under evaluation. Fuel cell Tafel curves have been measured using ion-exchange membranes in the leached state. Electroosmotic water transport measurements have been made observing the effect of pressure across the membrane.

4. -(1) Publications, Lectures, Reports and Conferences

a. Publications -

None

b. Reports -

Report No. 3 for this project
was submitted.

c. Conferences -

Conferences V was held on
21 February, 1963 at the Polytechnic Institute
of Brooklyn. Present were Mr. J. Perry of USAELRDL,
Mr. R. Danziger, Mr. R. Cooper and Dr. H. P. Gregor
of the Polytechnic Institute of Brooklyn.

d. Lectures -

None

5. Factual Data:

I. Resistance Cell:

A modified resistance cell was designed and is being built. This cell will furnish greater sensitivity in measurements of high conductance ion-exchange membranes. The new cell will bring the platinum electrodes one-sixteenth of an inch from the membrane surface.

The conventional cells have electrodes about 0.25 to 0.5 inches from the membrane surface. When low ($< 1 \text{ ohm} - \text{cm}^2$) resistance membranes are being measured, an appreciable error occurs because one is taking small differences between two large numbers.

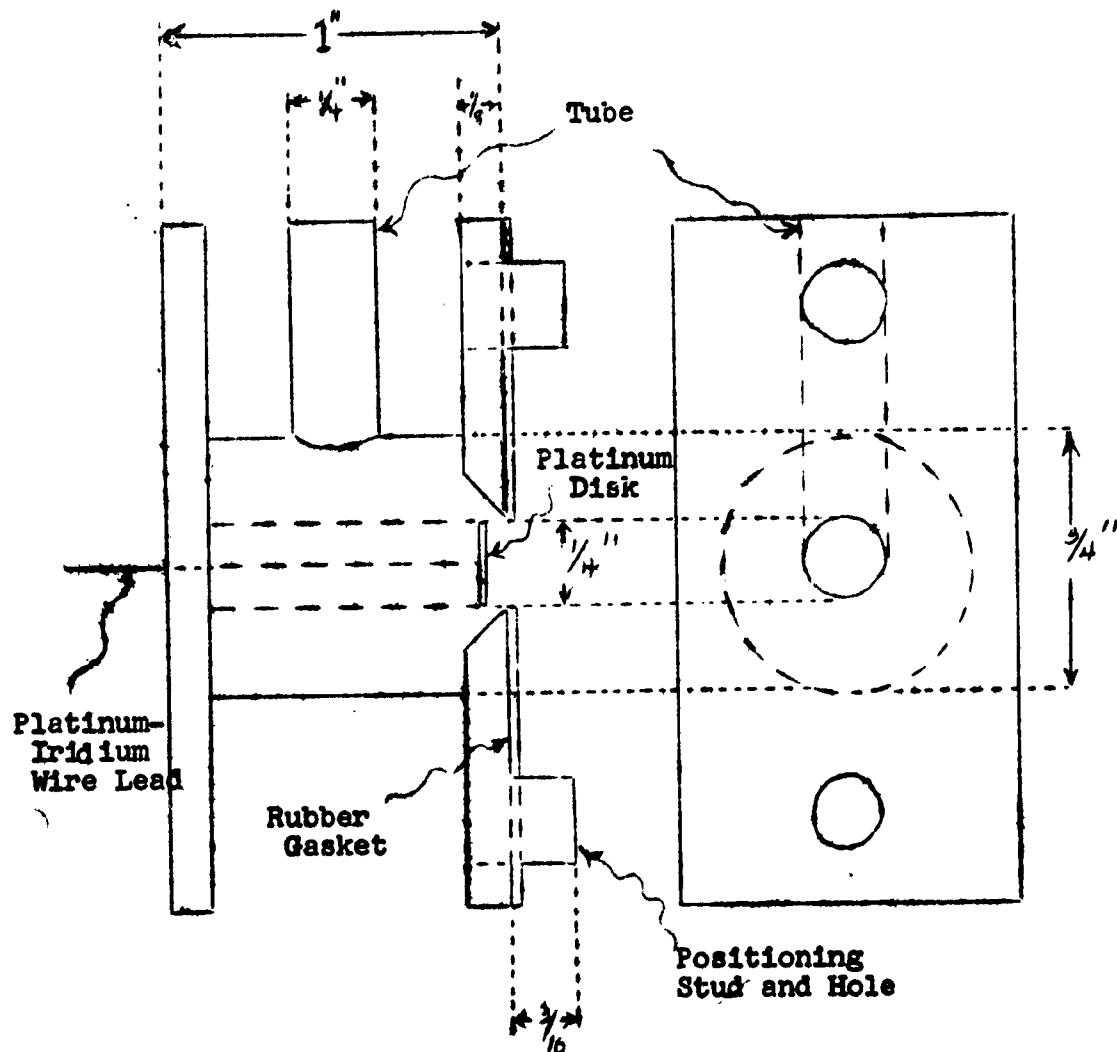
With the improved cell, the cell blank, measured in 0.1 N KCl, will be about 10 ohms, while that with the membrane will be about 15 ohms. Since the Klett bridge reads to 0.1 ohm and can be estimated to 0.05 ohms, it is seen that reasonable accuracy will be attained.

Because of Joule heating during the measurement, provisions will be made to flow fresh, thermostatted solution across the membrane face by a minor modification of the cell.

The cell design is shown in Fig. 1.

Figure I.

MODIFIED RESISTANCE CELL



* All parts made of craze-resistant plexiglass

II. Water Transport Measurements:

The effect of pressure on electroosmotic water transport was studied. The apparatus used was similar to that used for electroosmotic water transport studies as described in previous reports. The only modification necessary was the attachment of a device to exert a differential pressure across the membrane. This is most conveniently done with a manometer and air pressure for the higher pressures, and by simply applying a known head of water to one side of the cell for the lower pressures. The membrane selected for the study was one that had relatively large water transport rates. Nalfilm 4, made by The Nalco Chemical Company of Chicago, was used because of its good selectivity and high water transport rates. The differential pressure was varied between zero and 10 inches Hg. Throughout that range, there was no detectable change in the water transport rate with pressure. Higher pressures were not attempted, due to danger of rupturing the film.

The design of a cell that will withstand higher pressures and thus extend the range of validity of our measurements is in progress.

Preliminary analysis indicates that the control of flooding in ion-exchange membranes used in fuel cells cannot be easily effected by controlling the differ-

ential pressure across the membrane, when using conventional ion-exchange films. The hydrodynamic resistance of these films is very high, due to their fine pore diameters (about 10° Å). For example, Gregor et al (J. Phys. Chem., 61, 141 (1957)) measured water flow rates by using a counter osmotic pressure. With a 5 ohm - cm^2 sulfonic membrane, rates of 1.7 ml. hr.^{-1} were observed for 100 cm.^2 of membrane area and a pressure of 25 atm. Therefore, the hydraulic permeability for this film was $1.5 \times 10^{-5} \text{ cm mm}^{-1} \text{ atm}^{-1}$.

Therefore, when a counter pressure of 10 inches Hg was applied (0.3 atm.), the rate would be $5 \times 10^{-6} \text{ cm mm}^{-1}$. With the Nalfilm 4 membrane, the electroosmotic rate at 50 ma. cm.^{-2} was $2.5 \times 10^{-3} \text{ cm. mm}^{-1}$. Accordingly, a counter-pressure of 300 atms. would have been required to stop electroosmotic flow.

To allow one to control water transport rates by the imposition of a counter-pressure is not as difficult as might first appear, because hydraulic permeability varies as the fourth power of the pore radius, as an approximation. Some preliminary experiments with 100° Å pore membranes are in progress.

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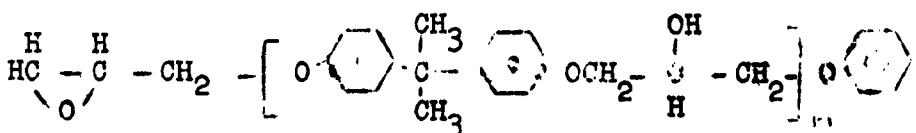
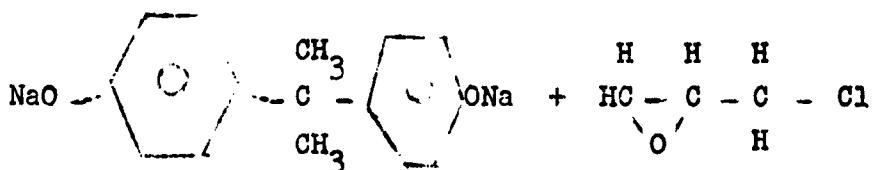
III. Preparation of Improved Membranes:

A. Reaction of Epoxy Resins with Sulfonic Acids.

It was observed that the onset of gelation in polymer solutions containing polystyrene sulfonic acid (PSA), a matrix polymer (either Kynar or Dynel) and bis-phenol-A type epoxy resins (Epon 828), in the absence of cross-linking agents, occurred very shortly after the combination of the reactants. Consequently, the mechanism of the reaction of sulfonic acids, polymeric as well as monofunctional analogues of benzenesulfonic acid, with epoxide groups were studied in order to assess the role of the latter in cross-linking reactions. In addition, various anhydride-type curing agents for epoxy resins were combined with Epon 828 alone to study the specific nature of any resultant cross-linking reactions. It is evident that if these casting solutions do not exhibit gelation in a comparable period of time under similar conditions in the absence of PSA, any contribution of these anhydrides toward a cross-linked system in the presence of PSA is negligible, or of secondary importance.

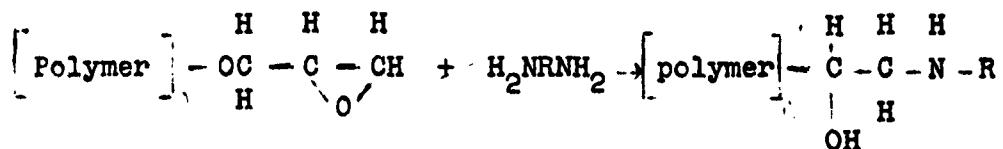
Before considering the reactions of epoxy resins with sulfonic acids, it is important to first review the nature of their reaction with the common curing agents.

The structure of epoxy resins and their reaction with various cross-linking agents are summarized below:

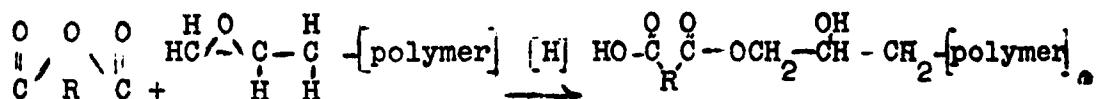


Here the sodium salt of bisphenol-A is reacted with an excess of epichlorohydrin resulting in a low molecular weight polymer where n is between 1 and 2, and which contains terminal epoxide groups. The commercial product Epon 828 is supplied in this form, and has an epoxide equivalent of 175-200. The term "epoxide equivalent" refers to the weight of resin which contains one equivalent of reactive epoxide groups.

A polyfunctional cross-linking agent such as a diamine, diacid or anhydride, reacts as follows:



In the presence of acid, anhydrides will react with the epoxide ring as follows:



Several other polyfunctional reagents may be added to the epoxy resins to yield a cross-linked network. The resulting systems are resistant to hydrolysis in both concentrated acid and base.

The addition of a fixed amount of PSA to a casting solution containing varying amounts of benzene-sulfonic acid (BSA) and a constant weight of epoxy resin resulted in progressively longer periods of time before gelation occurred in the systems containing large proportions of BSA.

Additional investigations were conducted with several conventional anhydride curing agents. No cross-linking occurred in these mixtures which contained just 828, BSA and the anhydride.

On the basis of these observations, it was concluded that the resultant gelation was due entirely to the reaction of the polymeric sulfonic acid with the epoxide groups to form sulfonate ester links. The presence of relatively large amounts of BSA prevented the PSA from

combining with a sufficient number of the remaining epoxide sites so as to form a gel structure.

The incorporations of flexibilizing agents into the epoxy system so as to render resultant films less brittle was also studied. One such material is Cardolite NC 513, essentially an epoxide joined to a long aliphatic chain (manufactured by the Irvington Varnish Division of Minnesota Mining and Manufacturing, Inc.).

NC-513 is always used in conjunction with epoxy resins in proportions not greater than 25%. Films were prepared using NC-513 which exhibited some of the properties of these materials.

B. Use of Phenol-formaldehyde Resins.

Along with the study of epoxy resins in the preparation of cross-linked cation-exchange membranes, phenol-formaldehyde resins were also studied. BRL-1100 is a material of this type; it is supplied as an approximately 65% solids content phenol-formaldehyde polycondensate in toluene, of moderate viscosity, supplied by the Bakelite Division of Union Carbide. In the past, this material has been used in anion-exchange membranes (see reports 3, 4 and 5, Contract No. DA-36-039 SC 85384). Phenol-formaldehyde resins are well suited to application

in PSA systems because the presence of acid (as well as heat) catalyses of the low molecular weight commercial product.

The resultant cross-linked polymer, with aromatic rings united by methylene or oxydimethylene bridges, would be expected to be rather brittle, but chemically stable in acid and dilute alkali solutions. However, since the cross-linked area bridges only molecular distances or intermicellar distances, the overall effect is not to import brittleness.

C. Results of Membrane Preparation Studies.

Table I lists the properties of a number of membranes. The tabular headings are consistent with conventions adopted in previous reports.

TABLE I

No.	<u>M</u> <u>g.</u>	<u>P</u> <u>g.</u>	<u>Solv.</u> <u>ml.</u>	<u>R₂</u> <u>ohm cm²</u>	<u>Co. P</u> <u>mV.</u>	Capacity meq./gr.	Remarks
BRL-I	BRL 0.67	PSA 0.5	DMF 7.0	59.7	12.41	0.82	Transparent, surprisingly flexible film.
251	DYNEL 0.75	PSA 0.6	DMF 12	0.35	10.40	0.325	Very soft film. Tears easily. Highly swollen.
	829 0.2						
	NC 513 0.05						
252	KYNAR 0.75	PSA 0.6	DMF 12	1.4	14.13	0.83	Translucent, flexible film.
	828 0.2						
	NC 513 0.05						
253	KYNAR 0.8	PSA 0.6	DMF 16	4.0	15.40		Sturdy, translucent film.
	BRL 0.33						
254	DYNEL 1.0	PSA 0.6	DMF 14	5.0	15.56		Sturdy, translucent film.
	BRL 0.33						
B-1	BRL 0.20	PSA 0.5	DMF 5				Film falls apart in water.
B-2	BRL 0.30	PSA 0.5	DMF 5				" " " " "
B-3	BRL 0.40	PSA 0.5	DMF 5				" " " " "
B-4	BRL 0.50	PSA 0.5	DMF 5				" " " " "

TABLE I - 2

No.	$\frac{M}{g}$	$\frac{P}{g}$	Solv. $\frac{ml}{g}$	R_2 ohm $\frac{cm}{mv.}$	Co. P. $mv.$	Capacity meq./gm.	Remarks
B-9	BRL 0.40	PSA 0.5	DMF 3.5	0.7	15.80		Films are strong, brittle.
B-8	BRL 0.47	PSA 0.5	DMF 3.5	0.6	15.43	" " "	"
B-20	BRL 0.52	PSA 0.5	DMF 3.5	0.6			Weak, fragile film.
B-19	BRL 0.60	PSA 0.5	DMF 3.5	7.2			Strong, sturdy film.
B-11	BRL 0.65	PSA 0.5	DMF 3.5	7.0		" " "	"
B-5	KYNAR 0.80	PSA 0.83	DMF 12.5	3.3		" " "	"
BRL 0.35							
B-16	KYNAR 0.40	PSA 0.5	DMF 7	5.6		" " "	"
BRL 0.21							
B-6	BRL 0.22	PSA 1.0	DMF 12	41.6			Flexible, strong film but does not look homogeneous.
B-40	KYNAR 0.35	PSA 0.5	DMF 5.5	1.1	12.3		Film has fair mechanical properties, but is slightly inhomogeneous.
BRL 0.35							
B-41	KYNAR 0.60	PSA 0.5	DMF 7	6.6	5.9		Slightly inhomogeneous, fair mechanical propert.
BRL 0.10							
B-42	KYNAR 0.10	PSA 0.5	DMF 5				Inhomogeneous, weak fragile film.
BRL 0.60							

TABLE I - 3

No.	$\frac{M}{g}$	$\frac{P}{g}$	Solv.	R_{cm^2}	$\frac{Co. P}{mV}$	Capacity $meq/gm.$	Remarks
B-43	KYNAR 0.30 BRL 0.30	PSA 0.5	DMF 6	1.6	12.7	"	Inhomogeneous, weak fragile film.
B-44	KYNAR 0.25 BRL 0.25	PSA 0.5	DMF 5	3.1	8.7	"	Slightly inhomogeneous.
B-45	KYNAR 0.8	PSA 0.5	DMF 8	11.3	6.7	"	Homogeneous - good mech- anical properties.
B-54	KYNAR 0.75 828 0.20 NC-513 0.05	PSA 0.5	DMF 7	1.6	12.0	"	Weak, fragile film.
B-55	KYNAR 0.50 828 0.25 NC-513 0.07	PSA 0.5	DMF 5	1.9	11.1	"	"
B-56	KYNAR 0.75 828 0.25	PSA 0.5	DMF 6	1.9	12.6	"	Good mechanical proper- ties - homogeneous.
B-57	KYNAR 1.0 828 0.33	PSA 0.5	DMF 9	3.9	12.9	"	"
B-58	KYNAR 0.75 828 0.10	PSA 0.5	DMF 7	1.4	14.7	"	"
B-59	KYNAR 0.75 828 0.12 NC 513 0.025	PSA 0.5	DMF 7	2.40	15.2	"	"

TABLE I - 4

No.	<u>M</u> <u>g</u>	<u>P</u> <u>g</u>	<u>Solv.</u> <u>mI</u>	<u>R</u> <u>ohm cm²</u>	<u>Co. P</u> <u>mv</u>	Capacity meq/gm.	Remarks
R-1	KYNAR 1.25 828 0.46	PSA 0.5	DMF 13	131			Fairly strong, in-elastic.
R-2	KYNAR 1.10 828 0.10	PSA 0.5	DMF 10	2.3	16.0		Strong, tough film.
R-3	KYNAR 1.0 828 0.20	PSA 0.5	DMF 10	2.0	15.35	" "	" "
R-4	KYNAR 0.88 828 0.33	PSA 0.5	DMF 11	111			Fairly strong; in-elastic film.
R-6	828 0.7	PSA 0.5	DMF 3				Extremely weak film.

17a

D. Mosaic Membranes.

Novel mosaic membranes have been made from a homogeneous, low resistance (0.1 gm. Epon 828-0.75 gm Kynar - 0.5 gm PSA- 7 ml DMF) formulation. The procedure consisted of casting the membrane with the doctor blade in the conventional manner, then curing it for a short time; the time varied between 10 minutes and one hour. The membranes were then sprayed with a fine mist of water to coagulate them and form large pores. The membranes were allowed to completely cure in this coagulated state. The membranes were then removed from the plate by soaking in water. They were then leached in methanol and soaked in a 10% solution of BPVI in methanol. The BPVI presumably filled the large pores, giving the membrane pores in which water transport was in a direction opposite to that of water transport by hydrogen ions. The methanol was evaporated and the membranes resoaked in water. The BPVI was presumably held in the membranes via charge neutralization with PSA. Concentration potential measurements have little meaning when applied to mosaic membranes. Since ions are conducted in both directions, a fairly low value is ordinarily obtained.

These mosaic membranes will be evaluated for water transport properties in the electroosmosis apparatus.

(IV. Fuel Cell Experiments.

Experiments were conducted on imprinting ion-exchange membranes and testing these in the leached state in fuel cells. Preliminary results indicate that there are some difficulties entailed in the use of our imprinting technique; possible improvements are now being considered.

The fuel cell apparatus consists of two stainless steel plates in a sandwich arrangement. These plates serve to hold in place two flow distributors which channel oxygen and hydrogen across opposite sides of the imprinted ion-exchange membrane. Expanded metal current collectors transfer current from the imprinting on the membrane to the flow distributors from which the current is withdrawn. The flow distributors are electrically insulated from each other and from the stainless steel plates by rubber gasket material which is bonded to the distributors.

The imprinting technique developed is similar to that described in Report 6 of Contract DA-36-039-SC-85384. Membranes were initially dried between platens of a Carver Press in such a manner that the membrane was flat and smooth. Platinum black was scattered evenly by the use of two four inch by four inch smooth-faced stainless steel plates, 1/8 of an inch thick and a third plate

of similar dimensions with a square 1 3/8 x 1 3/8 inches removed from the center, which served as a mask through which platinum black could be sprinkled. Flat teflon sheet 0.005 inches thick was then sandwiched between the lower plate and the steel mask. Care was taken that the catalyst was sprinkled evenly onto the membrane. A 100 mesh screen has been found convenient for this purpose, the screen being held a height of six inches from the membrane. Five to ten mg. of platinum was used for each square centimeter of exposed membrane area. The mask was placed over the membrane and a similar amount of catalyst is spread over the open face. The mask was then removed again, the membrane was covered by another teflon sheet, followed by the upper steel plate, thereby completing the "sandwich".

The thermally regulated platens of the hydraulic press were adjusted to approximately 100°C., and membranes were subjected to a force of 20,000 lbs. These conditions were maintained for two minutes. The "sandwich" was removed from the press. The teflon film surrounding the membrane prevented the platinum black from catalyzing reactions of the plastic membranes with air. After cooling, the membrane was equilibrated and reswollen in a distilled water bath. The imprinted membrane was then mounted inside the fuel cell. Care was

also taken that the stainless steel plates used to hold the cell together were parallel to one another and that the bolts were completely tightened. This was necessary in order to insure a good contact between the current collector and the imprinted membrane. The two gas chambers on either side of the membrane were then flushed with nitrogen before introducing the H₂ and O₂ to their respective chambers. This was done to prevent the reaction between the air and entering hydrogen.

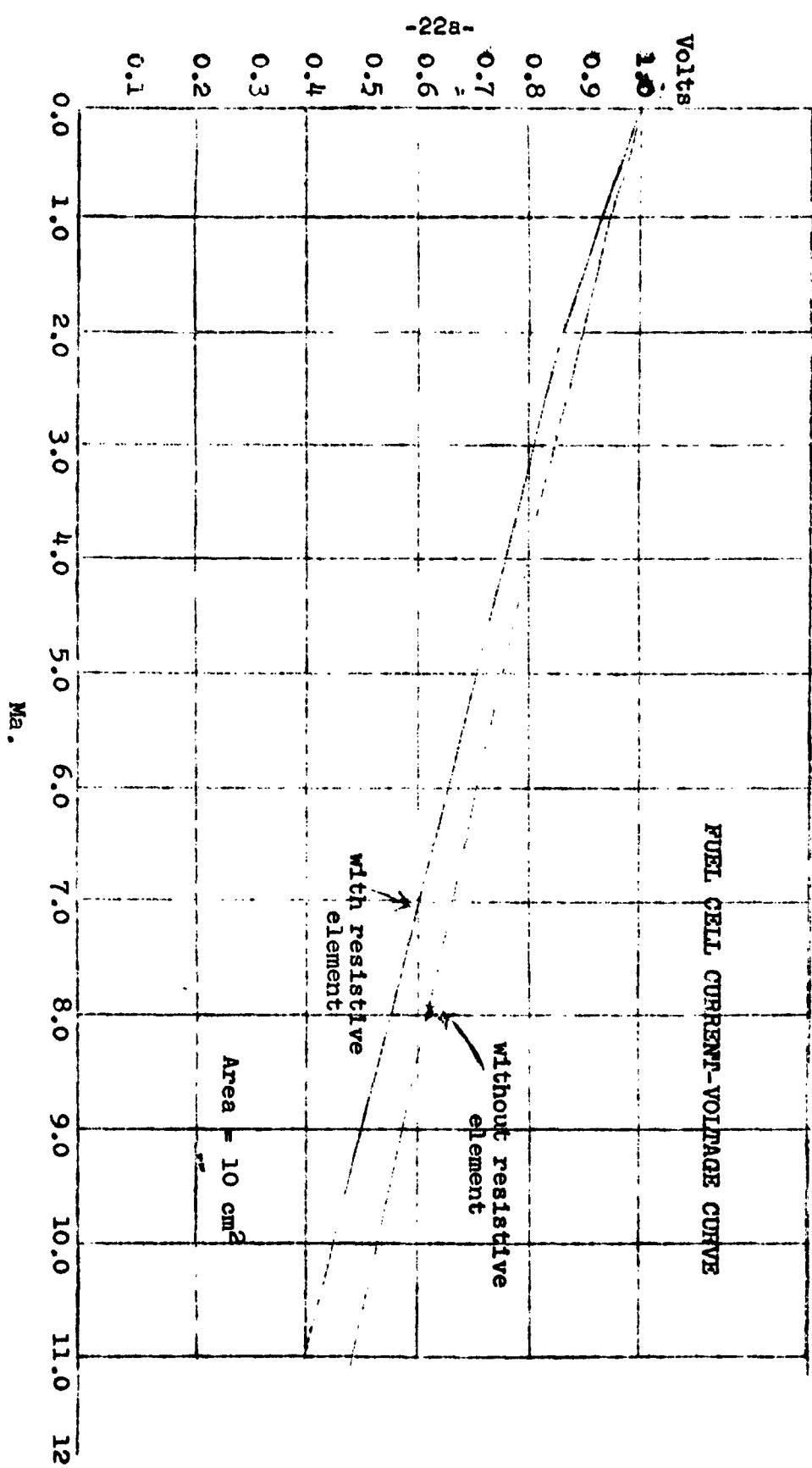
Several problems were encountered in the operation of the cell. Water transport proved to be a problem when non-mosaic membranes were used. It was observed that after long operating times that the performance of the cell would gradually decrease. This was also shown by the slow recovery after the application of heavy current.

The second difficulty encountered with the present procedure was the burning through of the membrane. After a certain time the ion-exchange membrane would become dark in a spot and a hole would develop. The subsequent mixing of the hydrogen and oxygen would quickly destroy the membrane. This was probably caused either by high, localized current densities or localized short circuits due to too deeply imbedded catalyst particles. There was no uniform pattern in the failures.

Sometimes they occurred immediately after the cell was started, sometimes after many hours of operation.

The current-voltage (Tafel) curve for an A.M.F. C-103 cation-exchange membrane is shown in Fig. 2. The sine wave interrupted pulse (Kondesh Marco) tester described in a previous report was used on the fuel cell and found to give a significantly higher current-voltage curve, indicating that the tester was working as designed. Minor changes were necessary in the tester in order to accurately maintain the smaller currents in the laboratory fuel cell. This curve is roughly similar to that reported for A.M.F. membranes in an earlier report. It is, however, considerably lower than that reported for more advanced imprinting techniques. In order to raise the performance of our cell and to get meaningful comparable numbers to completely characterize the best of our low resistance, low water transport membranes, it will be necessary to improve our imprinting technique. Variables such as the amount of graphite in the platinum, possible wet proofing for the catalyst, etc., remain to be investigated in this laboratory.

FIG. II



6. Conclusions

Table I lists the properties of various membranes utilizing the materials discussed in the previous sections. BRL-I is particularly interesting because besides its surprising lack of brittleness, the magnitudes of both the ionic resistance and concentration potentials in this heavily cross-linked system containing only BRL are not too far removed from desired levels.

As is indicated in Nos. 253 and 254, films with high selectivity and low resistance can be prepared using both Kynar and Dynel as matrix polymer, and BRL as the cross-linking agent.

Film No. 251 contains approximately the upper limit of polyelectrolyte to matrix polymer. This accounts for its poor strength, as well as high water permeability and low selectivity. The effect of NC-513 is seen more clearly in No. 252 which yielded a flexible but sturdy film accompanied by good electrical properties. Capacity measurements were also performed on several of the membranes listed in Table I. These measurements were performed in the conventional manner which entails the titration with standard base (under nitrogen) of the hydrogen ion displaced by a large excess of potassium ion (i.e., potassium chloride) from the film, originally

in acid form. The results listed are the averages of 2 measurements, which agreed with one another to within 5%.

Previous work has indicated that there is a maximum amount of PSA that can be contained in a given amount of Dynel or Kynar by the inter-polymer technique. It has, therefore, been necessary to perfect methods of holding the PSA in place in the membrane so that the membrane can contain a maximum amount of functional groups and hence have a low resistance and high selectivity.

It has been shown that it is possible to hold other poly-electrolytes in a stable film with excellent results by adding amounts of reactive polymer to cross-link the film. In the past period, research on homogeneous membranes has been directed towards perfecting the technology of cross-linked membranes using PSA as the poly-electrolyte. Two basic ways of cross-linking have been investigated. A neat curing phenol-formaldehyde resin (BRL-1100) as well as reactive epoxy resins with various types of curing agents have been used with Kynar and PSA to form some membranes that have very desirable properties. The neat cured phenol-formaldehyde (BRL) films were, in general, less satisfactory than the epoxy films with regard to both mechanical strength and electrical properties. It was found that small amounts of BRL did not

serve to hold the PSA in the membrane while it tended to give the membrane less desirable elastic and mechanical properties. It was evident that there was segregation of the phenol formaldehyde within the membrane so that there were small regions of pure phenol-formaldehyde surrounded by the Kynar. The pure BRL-PSA membranes had good electrical properties but were mechanically not highly flexible because of their highly cross-linked nature. With the epoxy films, high flexibility was attained. If small amounts of 828 were incorporated into the membrane, the desirable mechanical properties of the Kynar films were maintained yet the film was able to hold large amounts of PSA and, therefore, had a low resistance. PSA-Epoxy-Kynar membranes have been prepared which have desirable mechanical strength and toughness as well as good electrical properties.

Membrane Nos. B-1, 2, 3, 49, 8, 20, 19, and 11 are a study of the amount of PSA in pure BRL membranes. At the lower concentrations of PSA, satisfactory electrical properties were observed. The films were all somewhat brittle. Membrane Nos. B-40 to 45 were a study of various combinations of BRL, PSA and Kynar. These membranes were, in general, non-homogeneous and had mediocre physical and electrical properties. Films R1 to R6 and B-54 to B-59 were a study of various combinations of

Epon 828, PSA and Kynar. As can be seen, excellent mechanical and electrical properties were found with these films, especially those with smaller amounts of epoxy, e.g., Nos. B-58, 56, 59, R2, R4, etc.

7. Program for the Next Interval

- A. During the next interval, characterization of the homogeneous ion-exchange membranes will be carried out in 0.1 M HCl and distilled water as well as in 0.1 M KCl.
- B. Further investigations of fluorine-containing base polymers will be carried out.
- C. Current-voltage curves will be run on promising membranes.
- D. More mosaic membranes of various types will be synthesized.
- E. Characterization of membrane water transport properties will continue.

8. Identification of Personnel

H. P. Gregor, Project Supervisor, and Professor of Physical Chemistry at the Polytechnic Institute of Brooklyn - 170 hours.

R. M. Danziger, M. S. in Chemistry, Research Fellow at the Polytechnic Institute of Brooklyn - 413 hours.

R. A. Cooper, B. S. in Chemical Engineering, Research Fellow at the Polytechnic Institute of Brooklyn - 413 hours.

G. Brandrup, M. S. in Chemistry, Research Assistant at the Polytechnic Institute of Brooklyn - 85 hours.

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January 1963

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